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Physical characteristics of barium cadmium formate crystals

V Shettigar and S M Dharmaprakash
Department of Physics, Mangalore University, Mangalagangotri-574 199, Karnataka, India

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Abstract : Barium cadmium formate hydrate (BCF) crystals with molecular formula $Ba_{0.53}Cd_{0.47}(HCOO)_2.H_2O$ have been grown from aqueous solution by slow cooling. The grown crystals were characterized by atomic absorption spectrometry, X-ray diffraction, infrared spectral techniques. BCF crystallizes in monoclinic system with unit cell dimensions a = 13.611 Å; b = 13.241 Å, c = 11.887 Å, β = 31.9° and space group $P2_1/C$. UV vis IR spectra revealed that BCF crystals are optically transparent in the region 250–2100 nm. BCF is biaxial and is strongly anisotropic. Thermogravimetric analysis carried out on BCF indicate that the material is stable upto 95°C. The data of the electrical parameters combined with the thermal data was used to understand the mechanism of conduction. BCF crystals exhibit low defect concentration.

Keywords : Crystal growth, characterization

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1. Introduction

Crystals of formate family [1–5] exhibit marked nonlinear optical (NLO) properties. Of these, lithium formate hydrate together with a series of solid solution based on it, has the greatest optical nonlinearity and are widely used in quantum electronics. With an increasing demand of materials for nonlinear optical applications, investigations on crystallization and characterization of new materials are receiving great importance. The existence of barium-cadmium double formates with various phases in a wide range of barium formate and cadmium formate concentrations was indicated by Nadzharyan *et al* [6]. Eventhough barium cadmium formate single crystals were reported [7], the concentation of barium and cadmium in the grown material were not determined. The present paper reports on the physical characteristics of barium cadmium formate with molecular formula $Ba_{0.53}Cd_{0.47}(HCOO)_2.H_2O$.

2. Experimental

In order to investigate the crystallization condition of barium cadmium formate (BCF) pure phase, $(1-x)$ $Ba(HCOO)_2$ + (x) $Cd(HCOO)_2$ system in water was investigated at 30°C, where $x = 0.1, 0.2, \ldots, 0.9$. The solution yielded small plate like and needle like crystals in different experimental vessels after about 36 hours of solution evaporation at 30°C. Crystallization of new, pure and mixed phase were identified using atomic absorption spectrometry, thermal analysis, infrared and X-ray diffaction techniques. Pure phase single crystals of BCF resulted when the value of x was 0.5 in the solution system. For $x = 0.1$, along with barium formate and cadmium formate small traces of barium cadmium formate were present in the multiphase crystals. For the remaining x values along with BCF, cadmium formate and barium formate multiphase crystals were observed.

The presence of Ba^{2+}, Cd^{2+} and $(HCOO)_2$ in BCF were confirmed by the chemical analysis. The concentration of $Ba^{2+} = 0.53$ and $Cd^{2+} = 0.47$ (when $x = 0.5$) was estimated from the atomic absorption spectroscopy and hence the molecular formula for BCF is $Ba_{0.53}Cd_{0.47}(HCOO)_2.H_2O$. The solubility diagram of BCF is shown in Figure 1. The resultant data could be fitted to a curve following the equation $S = aT^2 + bT + c$, where S is

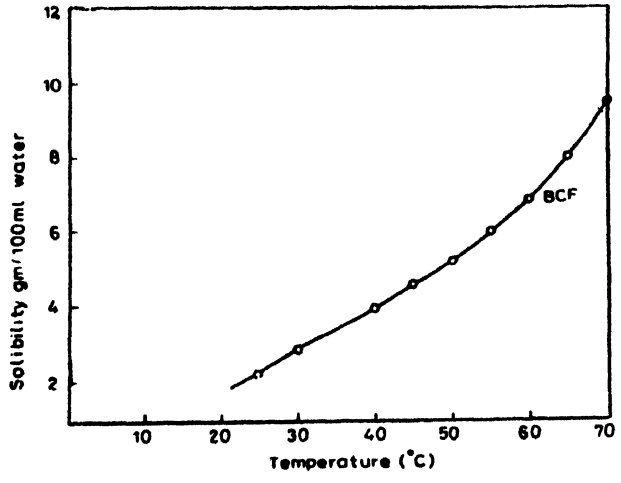

Figure 1. Solubility curve for BCF crystal in water.

the solubility expressed in gram/100 ml, T is the temperature in °C. The constants evaluated are $a = 0.0173$; $b = -0.01035$ and $c = 1.48036$. The temperature coefficient of solubility is positive. This indicates that slow cooling could be tried as a crystal growth method. Large single crystals of BCF were grown using solution growth technique, by means of mechanised cooling process between 50°C and 30°C. The resulting crystals were of the size (Figure 2) 35 × 12 × 14 mm^3. The growth rate of the crystal was high along 'C' axis and nearly equal along a and b directions. The growth velocities ranged between 0.2 and 0.4 mm/day.

Plate I

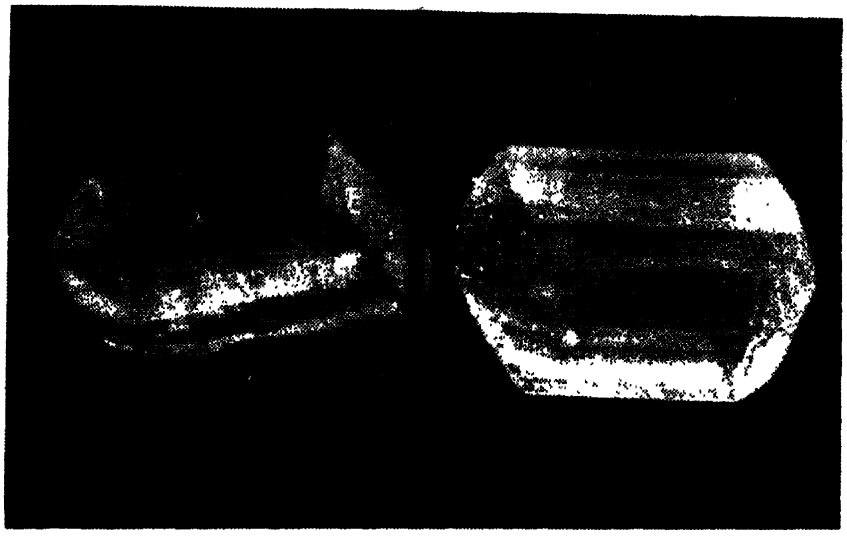

Figure 2. BCF single crystals.

3. Results and discussion

Powder X-ray diffraction pattern (Figure 3) of the grown crystal were obtained using Philips PM 9920 diffractometer with CuK_α radiation (λ = 1.5418 Å). Interplanar spacing '*d*' and (*hkl*) values for the palnes are indicated in the Figure 2. Single crystal X-ray diffraction

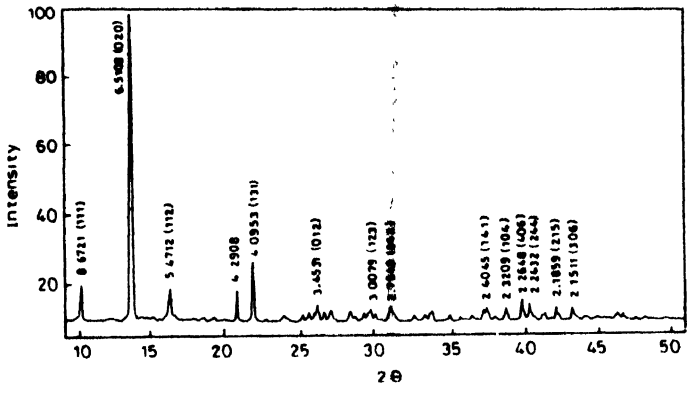

Figure 3. Powder X-ray diffraction pattern of BCF crystal

analysis was carried out using Enraf CAD 4 diffractometer. The unit cell dimensions of BCF are a = 13.611 Å; b = 13.241 Å; c = 11.887 Å; β = 31.9; z = 4; space group $P2_1/C$ and system monoclinic.

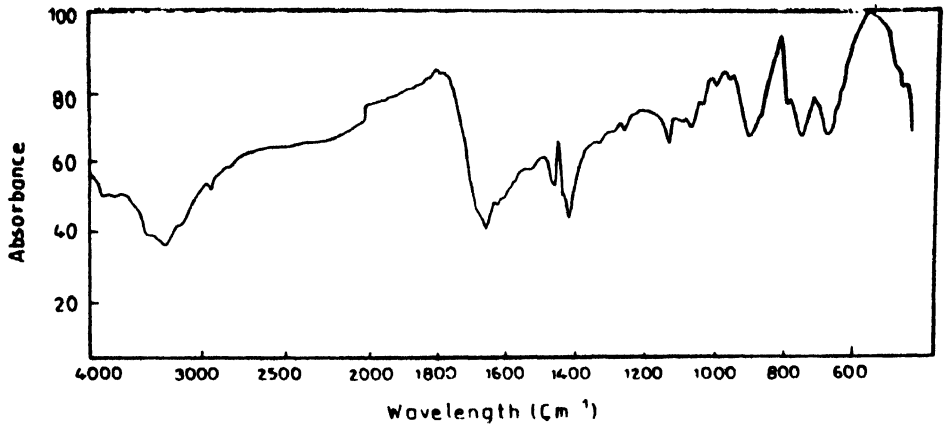

Figure 4. Infrared spectra of BCF crystal

Infrared spectra (Figure 4) for BCF crystals were recorded using Perkin Elmer spectrophotometer in the range 400–4000 cm^{-1}. The information obtained from the IR spectrm is summarised in Table 1. The absorption peaks correspond to the molecular group vibrations. According to the theories of infrared spectra [8] and the standard infrared spectra of metal formates [9], the relations of molecular group vibrations and the characteristic absorption bands were obtained.

A Metler TA 4000 thermal analyser system was used to study the thermal stability of BCF at a heating rate of 10°C/min in air. Figure 5 depicts the thermogravimetric analysis

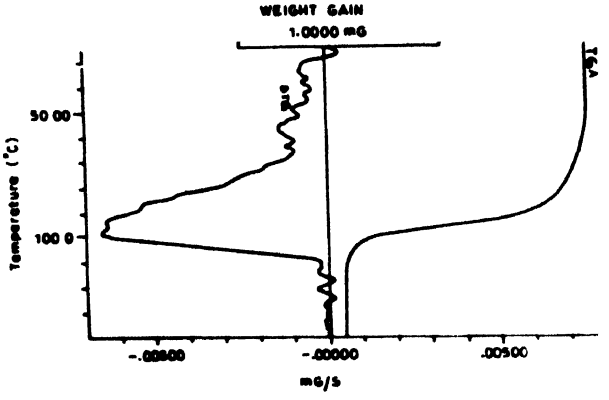

Figure 5. TGA and DTG curves for BCF crystal

(TGA) and differential thermogram (DTG) curves recorded simultaneously. Examination of the TGA and DTG curves indicates on the one hand the presence of crystallization water

Table 1. Assignment of infrared frequencies (cm^{-1}) for BCF crystal.

Description	Assignment	Frequency
O-H stretch	ν_1	2810, 2890
Symmetric OCO stretch	ν_2	1395, 1435, 1445
Symmetric OCO deformation	ν_3	750, 780
Asymmetric OCO stretch	ν_4	1630, 1660
Asymmetric OCO deformation	ν_5	1420, 1440
Out of plane C–H deformation	ν_6	1030, 1070 1090, 1130

molecule and on the other hand that the transformations are associated with mass changes and there is no physical transformations independent of mass change. From the curves it is clearly understood that BCF is stable upto 95°C. At this temperature it losses the water molecule from its lattice. Taking either the weight percentage of the end product or the initial weight as standard, the course of transition is analysed with reference to the molecular weight of BCF. It is observed that BCF contains one molecule of water of crystallization.

Figure 6 displays the optical transmission spectra of BCF single crystal with thickness 2 mm, recorded using a Hitachi U3400 UV *vis* IR spectrophotometer in the range 200–2200 nm. BCF is transparent in 250–1400 nm region. In the entire visible region the absorption coefficient is about 0.1. Three plates parallel to the crystal physical axis of BCF

were prepared for the determination of the refractive indices in the wavelength region 4000 Å – 7000 Å, by the Brewster's angle method [10]. Figure 7 shows the variation of refractive index with wavelength for BCF crystal. BCF is biaxial and strongly anisotropic.

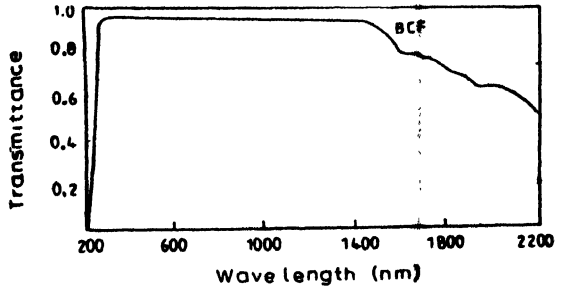

Figure 6. Optical transmission spectra of BCF single crystal.

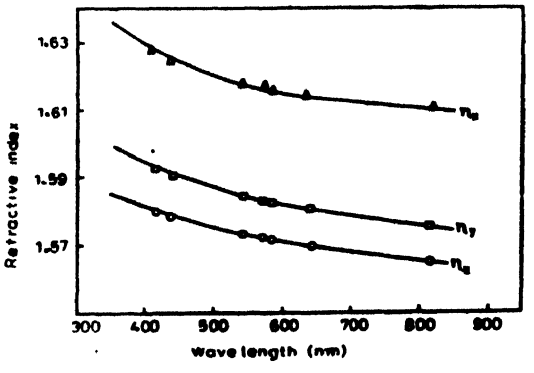

Figure 7. Variation of refractive index with wavelength.

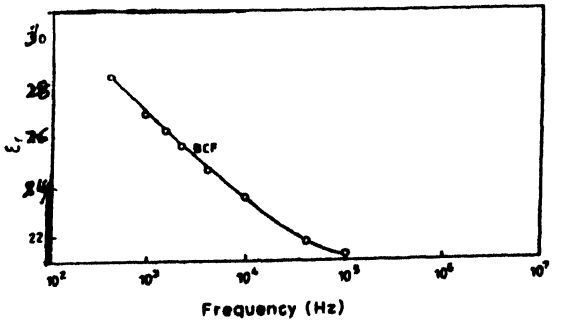

Figure 8. Variation of dielectric constant of BCF single crystal with frequency.

The electrical parameters such as dielectric constant, (Figure 8) and dielectric loss (Figure 9) of BCF single crystals perpendicular to *c*-axis were measured using an LCR

meter in the frequency range 1 KHz–4000 KHz at room temperature. The dielectric constant and dielectric loss decrease with increasing frequency. The variations observed at low frequencies are due to factors like impurities, grain boundaries and crystal defects [11].

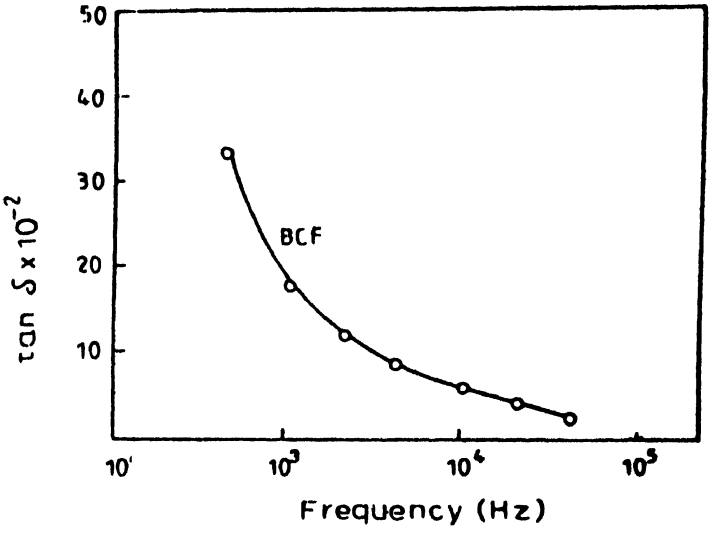

Figure 9. Variation of dielectric loss of BCF single crystal with frequency.

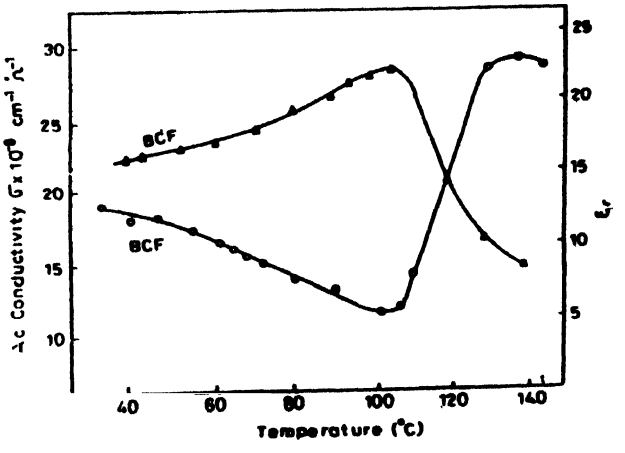

Figure 10. Variation of dielectric constant (Δ) and a.c. conductivity (0) with temperature.

Small value of dielectric loss in the BCF crystal indicates low concentration of defects in the material. The dielectric constant and a.c. conductivity (Figure 10) of BCF single crystals were also determined at varying temperatures in the range 27°C–150°C for 10 KHz. Considerable anamoly in the dielectric and conductivity values were not observed in the temperature region 30°C–90°C. There is a marked change in the dielectric and conductivity values at around 95°C, which is due to the dehydration of hydrated BCF into its anhydrous form. The dehydration temperature as determined from the conductivity measurements coincide with the dehydration peak values of BCF.

4. Conclusions

(1) Single crystals of barium cadmium formate with molecular formula $Ba_{0.53}Cd_{0.47}(HCOO)_2.H_2O$ have been grown from aqueous solution by slow cooling method.

(2) BCF crystallizes in the monoclinic system with space group $P2_1/C$.

(3) The results of thermal analysis indicate that the BCF crystals are thermally stable until about 95°C and there is no physical transformations independent of mass changes.

(4) X-ray powder diffraction reveals the crystallinity of the material.

(5) Small value of dielectric loss indicates low concentration of defects in BCF single crystal.

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